



Use of carbon felt cathodes for the electrochemical reclamation of urban treated wastewaters



Salvador Cotillas, Javier Llanos*, Manuel A. Rodrigo, Pablo Cañizares

Chemical Engineering Department, University of Castilla-La Mancha, Edificio Enrique Costa Novella, Campus Universitario s/n, 13005 Ciudad Real, Spain

ARTICLE INFO

Article history:

Received 12 May 2014

Received in revised form 27 June 2014

Accepted 1 July 2014

Available online 8 July 2014

Keywords:

Anode materials

Electrodisinfection

Electrochemical oxidation

Electro-Fenton

Carbon felt

ABSTRACT

This work focuses on the application of electrolysis with carbon felt cathodes for the reclamation of actual effluents from municipal wastewater treatment facilities (WWTFs) in combination with different anode materials (dimensionally stable anodes-DSA, conductive diamond anodes-CDA and iron-Fe). First of all, the efficiency of electrodisinfection with CDA and DSA was assessed, finding that total elimination of *Escherichia coli* (*E. coli*) can be attained at applied electric charges below 0.03 Ah dm^{-3} , and that the disinfection process is more efficient when using CDA. Furthermore, it was observed that the formation of hydrogen peroxide on carbon felt cathodes limits the concurrence of disinfection by-products (chlorates, perchlorates and organic chlorinated by-products), an interesting result that broadens the potential of CDA for the regeneration of urban wastewater. Results with Fe anodes show that it is possible to attain the complete removal of microorganisms with comparable efficiency to that of CDA (due to the contribution of Fenton's reaction) and that it was possible to totally remove the turbidity of the effluent when working at current densities from 12.50 A m^{-2} . Finally, it was found that Fe is the most efficient anode material (lowest power consumption) at low current densities and CDA is the most appropriate one at current densities higher than 5 A m^{-2} . According to these results, the pairs anode-cathode CDA-carbon felt and Fe-carbon felt behave as the most promising electrode materials to be applied in wastewater reclamation processes.

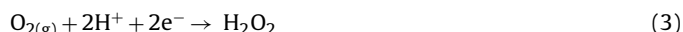
© 2014 Elsevier B.V. All rights reserved.

1. Introduction

Wastewater reuse has attracted great interest due to the potential uses of reclaimed wastewaters in agriculture or industry sectors and to the scarcity of fresh water sources [1–4]. In the reclamation of municipal wastewater, a disinfection stage is always required to obtain a high quality effluent as established by the Spanish legislation [5]. For this reason, many water disinfection technologies have been developed within the last years [6–8]. In this sense, several authors have reported the elimination of microorganisms, mainly *Escherichia coli*, by the addition of chemical reagents such as ozone, hydrogen peroxide or chlorine derivate products [9–12].

In this context, electrochemical technologies emerge as a good alternative to carry out the on-site generation of disinfectant agents from the species naturally contained in wastewater [13–17]. This production of disinfectants can be classified into anodic processes (i.e. the electrooxidation of chlorides to produce hypochlorite

[Eqs. (1) and (2)]) and cathodic processes (i.e. the electrochemical reduction of oxygen to produce hydrogen peroxide [Eq. (3)]).



The electrosynthesis of chloride oxoanions can be efficiently carried out by using anode materials such as dimensionally stable anodes (DSA) or conductive diamond anodes (CDA) [4]. These materials have exhibited great performance on the production of chlorine derivatives during the electrochemical treatment of wastewaters [18]. Regarding the electrochemical production of hydrogen peroxide, the search of new electrode materials to obtain higher production rates of hydrogen peroxide has become matter of interest for several authors [19,20]. Thus, carbon felt emerges as a promising cathode material to produce hydrogen peroxide in high concentrations [21–25] as this material presents higher specific area than other electrodes made of carbon such as carbon cloth or graphite.

When hydrogen peroxide is electrochemically produced on the cathode of an electrochemical cell, the use of iron as anode

* Corresponding author. Tel.: +34 926 29 53 00x3508; fax: +34 926 29 52 56.
E-mail address: javier.llanos@uclm.es (J. Llanos).

material can promote the well-known Fenton's reaction [26], producing hydroxyl radicals ($\cdot\text{OH}$) a powerful oxidant [Eq. (4)].



In addition, the use of iron anodes combined with the production of hydrogen peroxide, not only favors the Fenton's reaction, but also promotes coagulation processes from the generation of soluble and insoluble iron species. In this context, an interesting approach was carried out by Daghrir and Drogui [27], who described a combined electrocoagulation–electrofenton treatment for domestic wastewater using Ti– IrO_2 or iron as anode and graphite or vitreous carbon as cathode. With this system, it was possible to decrease efficiently the chemical oxygen demand (COD), turbidity and total suspended solids (TSS) in wastewater.

With this background, the main aim of the present work is to evaluate the efficiency of an electrochemical cell equipped with a carbon felt cathode and different anode materials (DSA, CDA and Fe) for the reclamation of actual effluents from municipal WWTFs, specifically, the elimination of *E. coli* and the removal of turbidity. In a first approach, the performance of the cell with commercial DSA and CDA was evaluated. Next, the anode was substituted by Fe, looking for the simultaneous removal of turbidity and microorganisms. For all anodes (DSA, CDA, iron), the effect of the current density on the process performance was studied and a first preliminary approach to the calculation of the energy consumption of the treatment process was also confronted.

2. Material and methods

2.1. Experimental setup

The electrodisinfection process was carried out in a batch electrochemical reactor. DSA (DSA- O_2 , DeNora, Italy), CDA (Adamant Technologies, Switzerland) and Iron (Fe) (Mervilab, Spain) were used as anodes and carbon felt (CF) (SGL Carbon, Spain) as cathode. DSA and Fe were rectangular with a geometric area of 80 cm^2 and CDA was circular with a geometric area of 68 cm^2 . CF was rectangular with dimensions of $14 \times 25\text{ cm}^2$ and a thickness of 1 cm. The electrode gap between anode and cathode was 75 mm. A power supply (0–30 V, 0–10 A) was used to apply current in electrodisinfection experiments (Delta Electronika ES030-10). To enhance the production of hydrogen peroxide, the wastewater was saturated by bubbling air into the reactor, maintaining a constant oxygen concentration of around 8 mg dm^{-3} during the electrodisinfection process. Wastewater was stored in a glass tank (5 dm^3), stirred by a magnetic stirrer (100 rpm).

2.2. Experimental procedure

Wastewater was collected daily at the secondary clarifiers of the WWTF of Ciudad Real (small town at the centre of Spain with 80,000 inhabitants). The influent of this municipal WWTF is domestic wastewater without a significant industrial contribution. Composition of the effluent sampled in terms of chemical parameters was very uniform. However, in terms of coliforms it varies significantly from day to day, as a consequence of the realistic conditions used. In spite of this, and after a SWOT (strengths, weaknesses, opportunities, and threats) analysis the use of any preservation method was discarded in order to assess purely the efficiency of the technologies studied. The average chemical and microbiological composition characteristics of the samples used in this work are shown in Table 1.

All experiments (3 dm^3) were carried out under galvanostatic conditions and discontinuous mode. At this mode of operation, the production of oxidant and disinfectant species is cumulative and it is related to the total Q (Ah dm^{-3}) applied at a given moment.

Table 1

Average composition of target wastewater.

Parameter	Value
Chloride (mg dm^{-3})	204.8
Nitrate (mg dm^{-3})	23.7
Sulphate (mg dm^{-3})	334.5
Ammonium (mg dm^{-3})	43.4
Iron (mg dm^{-3})	n.d.
Turbidity (NTU)	10–11
TOC (mg dm^{-3})	10.0
<i>E. coli</i> (CFU/0.1 dm^3)	2400–24,000

n.d.—Non detectable; TOC—total organic carbon.

The samples were collected in the glass tank and the sample volume was 0.1 dm^3 . The *E. coli* and disinfectant compounds (free and combined chlorine and hydrogen peroxide) were measured immediately. In this way, it is not necessary the addition of reagents (e.g. $\text{Na}_2\text{S}_2\text{O}_3$) to stop the reaction between microorganisms and disinfectants.

The current density applied ranged from 1.25 to 25 A m^{-2} . Prior to use in galvanostatic electrolysis assays, the electrode was cleaned for 10 min in a 5000 mg dm^{-3} Na_2SO_4 solution at pH 2 and 300 A m^{-2} to remove any kind of impurity from its surface.

2.3. Analytical techniques

The *E. coli* from wastewaters were estimated using the most probable number (MPN) technique [28] (confidence level: 95%). Microorganism counts were carried out by the multiple-tube-fermentation technique (24 h of incubation at 44°C) using five tubes at each dilution (1:10, 1:100, and 1:1000). After incubation time, the tubes with yellow color were considered positive (presence of *E. coli*) and the tubes in where the color remained red, were considered negative (absence of *E. coli*). The media culture used was E.C. MEDIUM ISO 7251 (the composition of the medium per liter of distilled water was 20 g dm^{-3} tryptose, 5 g dm^{-3} lactose, 1.9 g dm^{-3} bile salts no. 3, 4 g dm^{-3} K_2HPO_4 , 1.5 g dm^{-3} KH_2PO_4 and 5 g dm^{-3} NaCl) provided by Laboratorios Conda (Spain). For the determination of *E. coli*, 37.4 g of this reactive was dissolved in ultrapure water and were sterilized at 121°C during 10 min.

Nitrogen and chloride inorganic anions (NO_3^- , NO_2^- , Cl^- , ClO^- , ClO_2^- , ClO_3^- , ClO_4^-) were measured by ion chromatography using a Shimadzu LC-20A equipped with a Shodex IC I-524A column; mobile phase, 2.5 mM phthalic acid at pH 4.0; flow rate, $1 \times 10^{-3}\text{ dm}^3\text{ min}^{-1}$ (concentration accuracy: $\pm 0.5\%$). The peak corresponding to hypochlorite interferes with that of chloride; therefore, the determination of hypochlorite was carried out by titration with $0.001\text{ M As}_2\text{O}_3$ in 2.0 M NaOH [29,30]. This method consists of a redox determination to selectively quantify the hypochlorite concentration, specifically, it is based on the redox reaction between the hypochlorite and arsenite. Hypochlorite is reduced to chloride by the continuous addition of arsenite whereas this last one is oxidized to arsenate. The pretreatment of the samples consists of the addition of $2 \times 10^{-3}\text{ dm}^3$ of 2.0 M NaOH in order to increase the pH.

The same ion chromatography equipment (Shodex IC YK-421 column; mobile phase, 5.0 mM tartaric, 1.0 mM dipicolinic acid and 24.3 mM boric acid; flow rate, $1 \times 10^{-3}\text{ dm}^3\text{ min}^{-1}$) was used to measure the nitrogen inorganic cation (NH_4^+). Inorganic chloramines were measured following the DPD standard method described in the literature [28].

The presence of trihalomethanes (THMs) was evaluated by gas chromatography (detection limit $<0.2\text{ ppb}$) using a SPB 10 column ($30\text{ m} \times 0.25\text{ mm}$; macroporous particles with $0.25\text{ }\mu\text{m}$ diameter). Injection volume was set to $1 \times 10^{-6}\text{ dm}^3$.

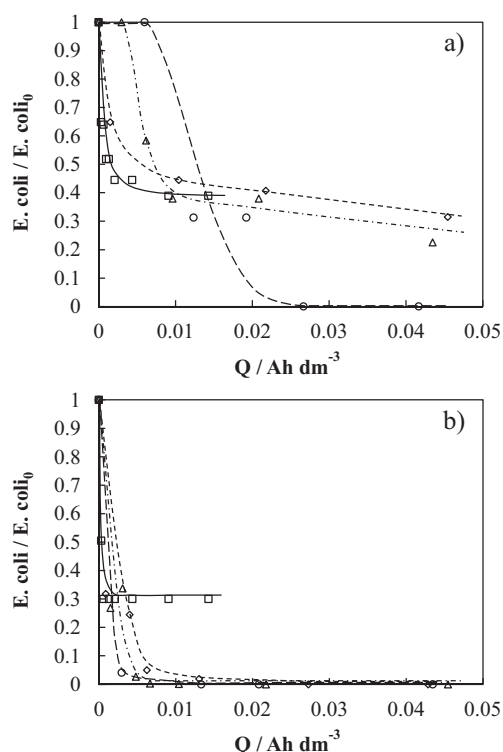


Fig. 1. Variation of *E. coli* with the applied electric charge at different current densities during the electrodisinfection process of urban wastewater. (a) Anode: DSA; \square 1.25 A m^{-2} ; $E. coli_0$: 5400 CFU/0.1 dm^3 ; pH: 8.4; \diamond 6.25 A m^{-2} ; $E. coli_0$: 5400 CFU/0.1 dm^3 ; pH: 8.7; \triangle 12.5 A m^{-2} ; $E. coli_0$: 24,000 CFU/0.1 dm^3 ; pH: 8.4; \circ 25 A m^{-2} ; $E. coli_0$: 2400 CFU/0.1 dm^3 ; pH: 8.4. (b) Anode: BDD; \square 1.46 A m^{-2} ; $E. coli_0$: 18,000 CFU/0.1 dm^3 ; pH: 8.5; \diamond 4.39 A m^{-2} ; $E. coli_0$: 22,000 CFU/0.1 dm^3 ; pH: 8.2; \triangle 7.32 A m^{-2} ; $E. coli_0$: 16,000 CFU/0.1 dm^3 ; pH: 8.3; \circ 14.63 A m^{-2} ; $E. coli_0$: 22,000 CFU/0.1 dm^3 ; pH: 8.51 (cathode: carbon felt; V: 3 dm^3 ; T: 25 $^\circ\text{C}$).

Hydrogen peroxide was measured according to Eisenberg [31]. This is a well-known colorimetric technique based on the reaction of hydrogen peroxide with a titanium sulphate reagent.

The total iron concentration was measured off-line using an inductively coupled plasma spectrometer (Liberty Sequential, Varian) (detection limit <1.5 ppb) according to a previously published standard method [28] (plasma emission spectroscopy). To evaluate the total metal concentration, samples were diluted to 50:50 (v/v) using 4 N HNO_3 to ensure total solubility of the metal.

Turbidity was measured using a 115 Velp Scientifica turbidimeter (measuring accuracy: $\pm 2\%$) according to a standard method described in the literature [28]. This measurement was carried out after sedimentation (30 min without agitation, typical settle time in reclamation of wastewaters) and filtration (0.45 μm filter) of the samples.

3. Results and discussion

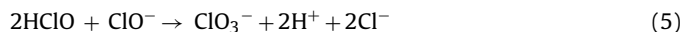
3.1. Electrochemical disinfection with carbon felt cathode and DSA/CDA

Fig. 1 shows the evolution of *E. coli* with the applied electric charge during the electrochemical disinfection process using DSA and CDA, at different values of current density.

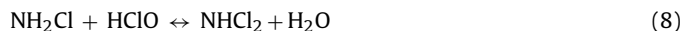
As it can be observed, it is possible to completely disinfect the target effluent at low values of current charge applied (lower than 0.03 Ah dm^{-3}). Experimental decay data follow an exponential decrease that may be fitted successfully to first order kinetic model. Regarding the current density, it is necessary a minimum value of 25 A m^{-2} to completely disinfect the wastewater using

DSA. However, it is possible to completely disinfect the effluent at a current density of 4.39 A m^{-2} when using CDA. For the same current density, charge required to deplete *E. coli* with CDA is lower than that necessary when using DSA. Taking into account that the average initial concentration in the experiments with CDA was higher (19,500 CFU/0.1 dm^3) than that with DSA (9300 CFU/0.1 dm^3), these results highlight the more efficient performance of CDA in terms of electrochemical disinfection. To explain this different behavior of both anode materials, it is important to note that the elimination of *E. coli* in wastewater is related to the attack to microorganisms of disinfectant species [18,32], electrochemically generated in the cell. Hence, the differences observed in the *E. coli* removal during the process with DSA and CDA should be explained by the different concentration (and/or type) of disinfectant species formed.

Chloride is one of the ions most commonly present in wastewater and its electrooxidation leads to the generation of hypochlorite, chlorate and perchlorate [33] (free chlorine) [Eqs. (1), (2), (5) and (6)]. Hypochlorite is known to exhibit a good disinfectant capacity but it can also form undesirable reaction by-products as trihalomethanes or other organochlorinated species [34,35]. In addition, the evolution of hypochlorite to chlorate and perchlorate [Eqs. (5) and (6)] in wastewater should be prevented, because of their detrimental effects to human health. At this point, it is important to note the effect of pH on chlorine speciation. In the tests carried out, the pH did not suffer important changes and it was kept almost constant around 8 during the complete process. These pH values favor the presence of ClO^- , taking into account the equilibrium of dissociation of HClO to ClO^- [Eq. (2)].



Furthermore, one of the reactions that most commonly takes place when hypochlorite is present in wastewater containing ammonium ions is the formation of inorganic chloramines (combined chlorine) [36]. Chloramines are formed by the chemical reaction between hypochlorite and the ammonium present in wastewater [Eqs. (7)–(9)]. The generation of these species mainly depend on the $\text{ClO}^-/\text{NH}_4^+$ ratio and the pH [37]. Chloramines are good disinfectants not as strong as hypochlorite, although they are less aggressive to human health than hypochlorite and, in addition, they prevent the formation of trihalomethanes.



Due to the importance of free and combined chlorine derivatives in the disinfection process, their concentration was monitored during the electrolyses. Figs. 2 and 3 show the evolution of hypochlorite and combined chlorine species during the electrodisinfection of urban wastewater with DSA and CDA, respectively.

As it can be observed, in all cases there is an initial increase in the hypochlorite concentration at low applied electric charges, followed by a decrease at higher values of electric charge, a typical profile of a reaction intermediate. Regarding the results obtained with DSA, the maximum concentration of hypochlorite increases with the applied current density. However, the production of hypochlorite is less efficient at the highest current density (25 A m^{-2}), probably due to the appearance of secondary side reactions at the higher potentials required to reach this value of current density.

The decrease of hypochlorite concentration may be related to several processes that simultaneously occur in the electrochemical cell: (1) the attack to *E. coli* (causing their death); (2) oxidation of hypochlorite to chlorate or perchlorate [Eqs. (5) and (6)];

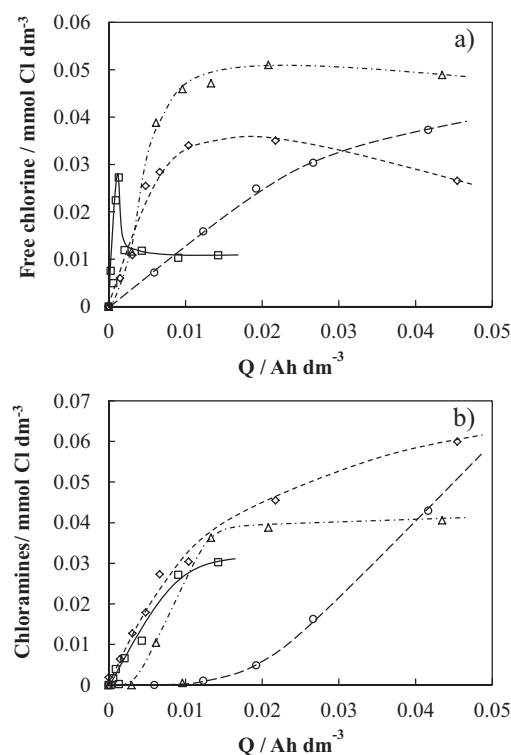


Fig. 2. (a) Evolution of free chlorine species with the applied electric charge during the electrodisinfection process of urban wastewater. (b) Evolution of combined chlorine species with the applied electric charge during the electrodisinfection process of urban wastewater (\square 1.25 A m⁻²; pH: 8.4; \diamond 6.25 A m⁻²; pH: 8.7; \triangle 12.5 A m⁻²; pH: 8.4; \circ 25 A m⁻²; pH: 8.4; Anode: DSA; cathode: carbon felt; V: 3 dm³; T: 25 °C).

(3) the reaction with other species such as ammonium [Eqs. (7)–(9)] to form chloramines. At this point, it is worth noting that neither chlorate nor perchlorate were detected within the range of current densities tested in the present work, so the oxidation of hypochlorite to chlorate or perchlorate can be discarded. On the contrary, the presence of chloramines has been detected during the electrodisinfection at different current densities with DSA (Fig. 2b). Concentration of chloramines increased with the electric charge and the applied current density, following a similar trend regardless the value of the current density. Nevertheless, a dissimilar profile is observed for the highest value of current density (25 A m⁻²) due to the less efficient production of hypochlorite previously described. Finally, it is important to note that the pH remained constant at about 8, a value that favors the formation of monochloramine.

Regarding the results observed for CDA (Fig. 3), the concentration of hypochlorite increases with the applied electric charge following a similar trend than that observed during the electrodisinfection with DSA: there is an initial increase in the concentration, followed by a decrease. However, the concentration of chloramines (Fig. 3b) increases with the applied electric charge and the current density, reaching higher concentrations than those obtained when working with DSA. These results seem to indicate that CDA favors the generation of combined chlorine species in wastewater and therefore, the disinfection of microorganisms by chloramination.

A somehow unexpected result is that neither chlorate nor perchlorate were detected in the electrodisinfection process using CDA. In this context, many authors have reported the formation of chlorate and perchlorate by CDA electrolyses in aqueous solutions containing chlorides [38–40]. However, a key differential aspect of the present work is the promotion of hydrogen peroxide production by the use of carbon felt cathodes and the bubbling of oxygen into the system. This fact suggests an important and unexpected role of hydrogen peroxide. It is well known that hydrogen peroxide

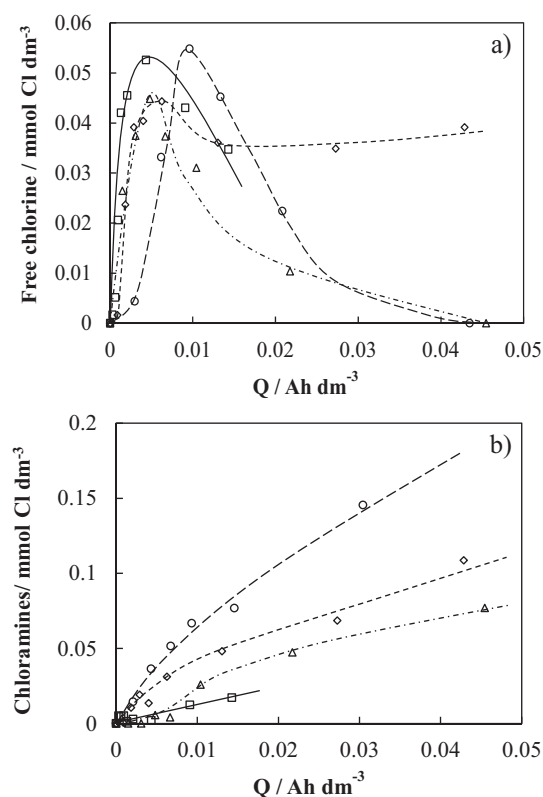
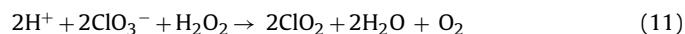
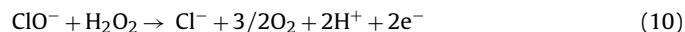


Fig. 3. (a) Evolution of free chlorine species with the applied electric charge during the electrodisinfection process of urban wastewater. (b) Evolution of combined chlorine species with the applied electric charge during the electrodisinfection process of urban wastewater (\square 1.46 A m⁻²; pH: 8.5; \diamond 4.39 A m⁻²; pH: 8.2; \triangle 7.32 A m⁻²; pH: 8.3; \circ 14.63 A m⁻²; pH: 8.51; Anode: BDD; cathode: carbon felt; V: 3 dm³; T: 25 °C).

can act as oxidant or reductant depending on the composition of the reaction media. Thus, hydrogen peroxide may react with hypochlorite, causing its reduction to chloride [Eq. (10)], and with chlorate to form chlorine dioxide [Eq. (11)], a reaction studied by Crump et al. [41].



This latter reaction leads to the formation of chlorine dioxide, an excellent disinfectant with no tendency to form disinfection by-products, and may take place preferentially near the anode surface due to the local acidic pH formed by the water oxidation reaction [Eq. (12)].



Due to these reactions, the occurrence of hazardous disinfection by-products in the treated effluent (chlorate or organic chlorinated by-products) will be limited due to the reductant behavior of hydrogen peroxide. This fact can broaden the potential applications of CDA to the reclamation of wastewaters, allowing to work at higher current densities and thus reaching higher disinfection rates without the production of hazardous disinfection by-products.

The evolution of hydrogen peroxide is showed in Fig. 4. As it can be observed, the concentration of hydrogen peroxide increases with the applied electric charge due to the reaction of oxygen reduction. Furthermore, the profile of hydrogen peroxide production is similar when using CDA and DSA as anode materials. This result is somehow expected taking into account that the production of hydrogen peroxide is a cathodic process. Regarding the influence of current density, it can be observed that the efficiency in

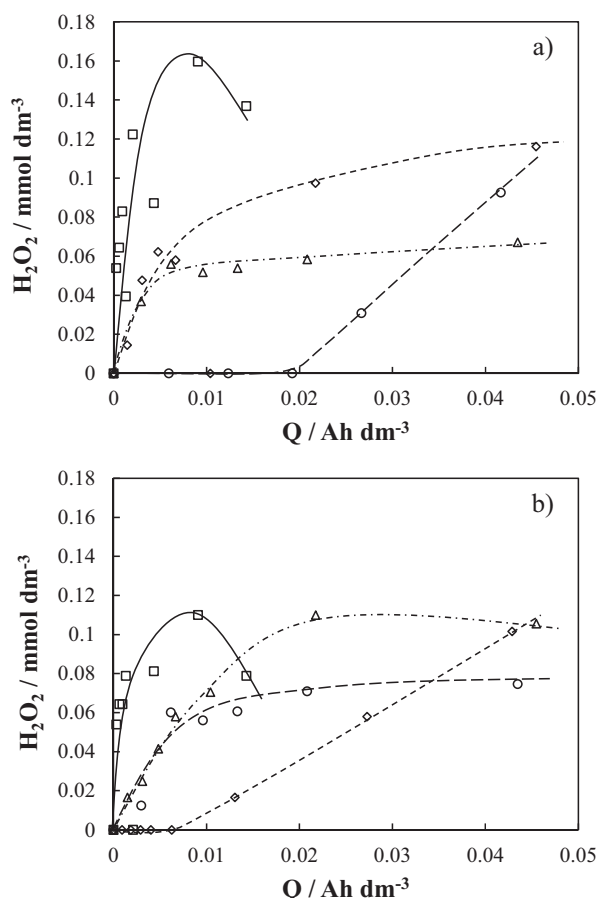


Fig. 4. Evolution of hydrogen peroxide with the applied electric charge during the electrodisinfection process of urban wastewater. (a) \square 1.25 A m^{-2} ; pH: 8.4; \diamond 6.25 A m^{-2} ; pH: 8.7; Δ 12.5 A m^{-2} ; pH: 8.4; \circ 25 A m^{-2} ; pH: 8.4; Anode: DSA; cathode: carbon felt; V: 3 dm^3 ; T: 25°C . (b) \square 1.46 A m^{-2} ; pH: 8.5; \diamond 4.39 A m^{-2} ; pH: 8.2; Δ 7.32 A m^{-2} ; pH: 8.3; \circ 14.63 A m^{-2} ; pH: 8.51; Anode: BDD; cathode: carbon felt; V: 3 dm^3 ; T: 25°C .

the production of hydrogen peroxide decreases for higher values of current density (lower concentration of hydrogen peroxide for the same value of electric charge applied). This result can be explained in terms of the oxidation/reduction of hydrogen peroxide on the surface of the electrodes. In fact, the use of current densities higher than 10 A m^{-2} is not recommended for hydrogen peroxide production because of the promoted oxidation and reduction of hydrogen peroxide on the electrodes surface [Eqs. (13) and (14)] [42].



Regarding the anionic nitrogen species, the concentration of NO_3^- was monitored during the process and it was found that this compound remained constant in its initial value (around 23 mg dm^{-3}). On the other hand, NO_2^- was under the detection limit throughout the tests.

As it has been described, the disinfection efficiency of the process and the production of hydrogen peroxide have been demonstrated in this first approach of the work. However, the minimum current density necessary to completely eliminate the microbiological content in wastewater is higher with DSA than with CDA (25 for DSA vs. 4.39 A m^{-2} for CDA). The next step that has been proposed is the use of Fe anodes in order to evaluate the promotion of Fenton's reaction [43,44] as well as the potential removal of turbidity by the generation of both soluble and non-soluble iron species.

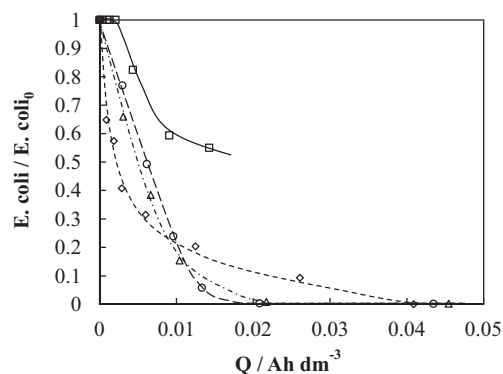
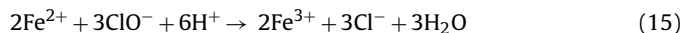


Fig. 5. Variation of *E. coli* with the applied electric charge at different current densities during the electrodisinfection process of urban wastewater (\square 1.25 A m^{-2} ; *E. coli*₀: $9100 \text{ CFU}/0.1 \text{ dm}^3$; pH: 8.5; \diamond 3.75 A m^{-2} ; *E. coli*₀: $5400 \text{ CFU}/0.1 \text{ dm}^3$; pH: 8.5; Δ 6.25 A m^{-2} ; *E. coli*₀: $9100 \text{ CFU}/0.1 \text{ dm}^3$; pH: 8.4; \circ 12.5 A m^{-2} ; *E. coli*₀: $13,000 \text{ CFU}/0.1 \text{ dm}^3$; pH: 8.2). Anode: Fe; cathode: carbon felt; V: 3 dm^3 ; T: 25°C .

3.2. Electrochemical disinfection of urban wastewater with Fe anodes

Fig. 5 shows the evolution of *E. coli* with the applied electric charge during the electrodisinfection of urban wastewater at different current densities, using iron as anode and carbon felt as cathode. As it can be observed, the concentration of microorganisms decreases with the applied electric charge, reaching a total removal of *E. coli* from current densities of 3.75 A m^{-2} . This current density is similar to the minimum value necessary to completely remove the microbiological content with CDA, but considerably lower than that for DSA. This behavior should be related to the mediated reactions that take place in the cell and it can result in the disinfection of the effluent: (1) reaction of free and combined chlorine species with *E. coli*; (2) oxidation of *E. coli* by hydrogen peroxide and/or hydroxyl radicals produced through Fenton's reaction [Eq. (4)]. In addition, the microorganisms can be removed enmeshed in the flocs generated by the dissolution of the anode material during the process.

As observed in Fig. 6, hypochlorite increases with the applied electric charge following the same trend than that observed during the process with DSA and CDA. However, the maximum concentration achieved of free chlorine is considerably lower when using Fe anodes. In addition, it has been observed that hypochlorite concentration is almost null at very low current densities. This behavior can be related to the reaction of hypochlorite with the generated Fe^{2+} , to form Fe^{3+} [Eq. (15)].



Regarding the combined chlorine, its concentration decreases when iron is used as anode as compared when DSA or CDA are used in the electrolytic cell, although it has been observed significant concentrations of chloramines for all current densities studied. This fact indicates that the elimination of *E. coli* by chlorine derivatives is mainly due to chloramines and not to hypochlorite, an interesting result due to the less aggressive behavior of chloramines in disinfection processes, previously described. Likewise, the presence of chlorate, perchlorate and trihalomethanes was not detected within the entire range of current densities tested.

Next, the concentration of hydrogen peroxide was also measured and it is represented in Fig. 7. As it can be observed, the concentration of hydrogen peroxide is similar to that measured when using CDA and DSA. As it has been previously commented, the production of hydrogen peroxide is a cathodic process and similar concentrations in the reactor should be expected for different anode materials. Nevertheless, the use of iron as anode material

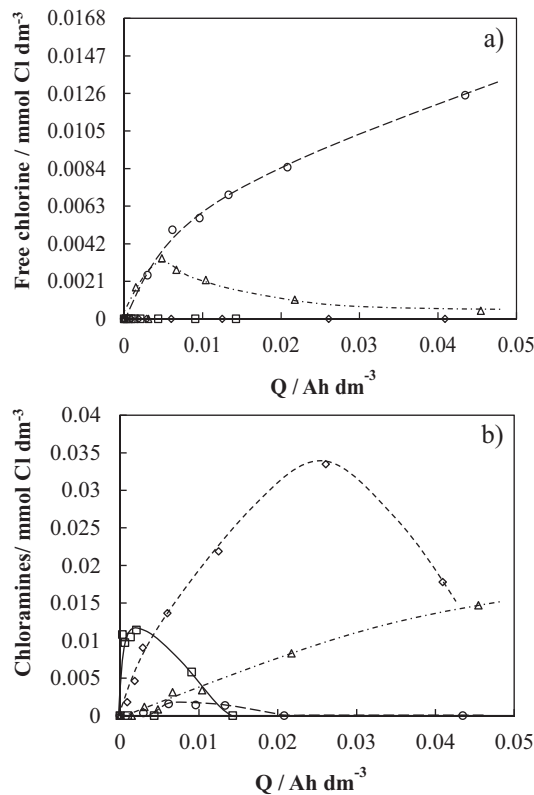


Fig. 6. (a) Evolution of free chlorine species with the applied electric charge during the electrodisinfection process of urban wastewater. (b) Evolution of combined chlorine species with the applied electric charge during the electrodisinfection process of urban wastewater (\square 1.25 A m⁻²; pH: 8.5; \diamond 3.75 A m⁻²; pH: 8.5; \triangle 6.25 A m⁻²; pH: 8.4; \circ 12.5 A m⁻²; pH: 8.2). Anode: Fe; cathode: carbon felt; V: 3 dm³; T: 25 °C.

leads to the generation of iron species (Fe²⁺), which can react with the hydrogen peroxide to produce hydroxyl radicals [Eq. (4)], with a higher oxidation power to eliminate the microorganisms. This reaction can explain the higher efficiency of the electrodisinfection process when using Fe compared to that reached with DSA. In addition, the promotion of Fenton's reaction can enhance side oxidation processes, as the removal of dissolved organic matter, in the treated effluent [45,46]. The similar concentration of hydrogen peroxide measured for different anodes may indicate that the

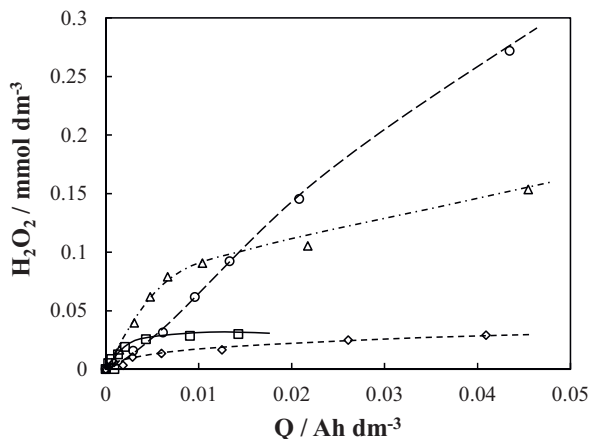


Fig. 7. Evolution of hydrogen peroxide with the applied electric charge during the electrodisinfection process of urban wastewater (\square 1.25 A m⁻²; pH: 8.5; \diamond 3.75 A m⁻²; pH: 8.5; \triangle 6.25 A m⁻²; pH: 8.4; \circ 12.5 A m⁻²; pH: 8.2). Anode: Fe; cathode: carbon felt; V: 3 dm³; T: 25 °C.

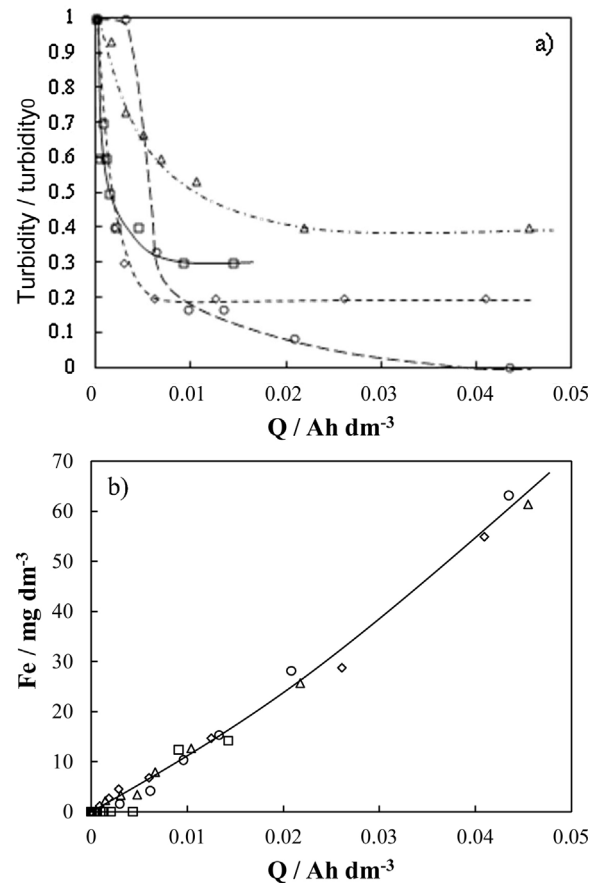


Fig. 8. (a) Evolution of turbidity with the applied electric charge during the electrodisinfection process of urban wastewater. (b) Evolution of total iron concentration with the applied electric charge during the electrodisinfection process of urban wastewater (\square 1.25 A m⁻²; turbidity₀: 10 NTU; pH: 8.5; \diamond 3.75 A m⁻²; turbidity₀: 10 NTU; pH: 8.5; \triangle 6.25 A m⁻²; turbidity₀: 11 NTU; pH: 8.4; \circ 12.5 A m⁻²; turbidity₀: 12 NTU; pH: 8.2). Anode: Fe; cathode: carbon felt; V: 3 dm³; T: 25 °C.

oxidation of hydrogen peroxide on the anode surface (Eq. (13)) is much significant when using DSA or CDA than for iron.

On the other hand, the electrodisinfection of the anode causes the generation of soluble and insoluble iron species [Eqs. (16)–(23)], which can act as coagulant species (mainly Fe(OH)₃) favoring the removal of turbidity in wastewater. This process is known as electrocoagulation (EC).

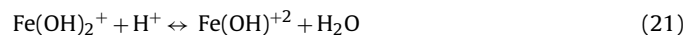
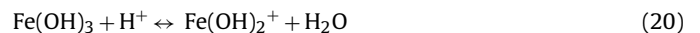
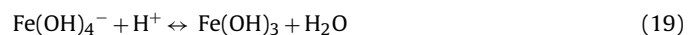
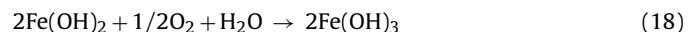
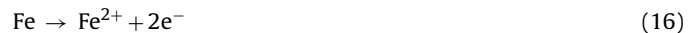


Fig. 8 shows the evolution of turbidity (Fig. 8a) and total iron concentration (Fig. 8b) with the applied electric charge during the electrochemical disinfection with iron anodes. As it can be observed, turbidity decreases with the applied electric charge and the current density. This enhanced performance is due to the higher efficiency of the electrodisinfection of the anode. In this way, the final total iron concentration increases from 14.23

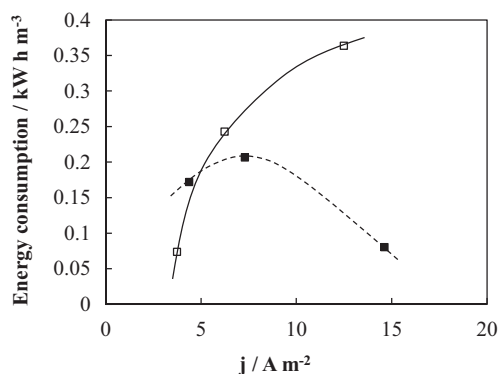


Fig. 9. Variation of energy consumption with the applied current density during the electrodisinfection process of urban wastewater (■) Anode: BDD; (□) Anode: Fe, cathode: carbon felt; V: 3 dm³; T: 25 °C.

to 63.21 mg dm⁻³ when the current density increases from 1.25 to 12.5 A m⁻². Furthermore, it is possible to attain the complete removal of turbidity in wastewater when working at current densities of 12.50 A m⁻².

The nature of the iron species formed depends mainly on the pH and metal concentration of the wastewater [47,48]. In this context, the pH was naturally maintained at approximately 8 during the experiments. Thus, under these operating conditions and according to the literature cited above, the dominant coagulant species are insoluble hydroxide precipitates, and the mechanism of coagulation should be sweep flocculation.

This behavior observed during the electrodisinfection with iron electrodes indicates that the use of iron as anode material and carbon felt as cathode material not only allows removing the microbiological content in wastewater, but also the removal of turbidity. Thus, it is possible to integrate in only one experimental set-up with the Electro-Fenton process the two main goals looked for reclamation.

3.3. Energy consumption during the electrochemical treatment of urban wastewater

In this section, the energy consumption per unit volume was calculated by means of the specific electrical charge passed (Q , kAh m⁻³) and the average total applied voltage (V , V) [Eq. (24)].

$$W \text{ (kWh m}^{-3}\text{)} = Q \times V \quad (24)$$

The energy consumption was calculated for the minimum applied electric charge in which the *E. coli* was completely removed. Fig. 9 shows the energy consumption at different current densities during the electrochemical disinfection with CDA and iron electrodes. As it can be observed, the energy consumption is lower than 0.2 kWh m⁻³ during the process with CDA, regardless the current density applied. However, there is an initial increase in the power consumption followed by a decrease with the applied current density. This fact is due to that the use of higher current densities (14.63 A m⁻²) requires lower electric charges (0.0062 Ah dm⁻³) to completely disinfect the wastewater. Regarding iron anodes, the energy consumption increases with the current density applied. In this case, the increased energy consumption with iron anodes is mainly due to the increase in electric potentials generated by the high applied current densities, probably due to the progressive deterioration of the electrode throughout the tests. Likewise, it is important to note that the energy consumption required with 12.50 A m⁻² (0.3636 kWh m⁻³) not only allows to eliminate the *E. coli* concentration, but also a complete turbidity removal is achieved in wastewater.

On the other hand, the energy consumption required during the process with DSA is 0.3040 kWh m⁻³. This anode only allows the total disinfection of wastewater at current density of 25 A m⁻² with an applied electric charge of 0.0267 Ah dm⁻³ and therefore, the data for lower current densities has not been calculated.

As a conclusion, these results seem to indicate that, in terms of power consumption, iron is the most appropriate anode material to carry out the electrodisinfection process at very low values of current density. On the contrary, CDA is the most appropriate for the electrodisinfection of urban wastewater at current densities higher than 5 A m⁻².

4. Conclusions

From this work, the following conclusions can be drawn:

- The use of carbon felt as cathode material and DSA or CDA allows to completely disinfect urban treated wastewaters at low current densities. However, the minimum current density necessary to completely eliminate the microbiological content in wastewater is higher with DSA (25 for DSA vs. 4.39 A m⁻² for CDA).
- Hypochlorite, chloramines and hydrogen peroxide have been identified as the main compounds responsible for the disinfection process with DSA/CDA anodes and carbon felt cathodes. In addition, the presence of trihalomethanes and chlorine compounds in high oxidation state has been discarded for all the current densities studied.
- The production of hydrogen peroxide avoids the formation of chlorate, perchlorate and organic chlorinated by-products during the disinfection process with CDA, as it reacts with hypochlorite to form chloride and with chlorate to produce chlorine dioxide. This behavior broadens the applications of CDA, allowing to work at higher current densities than those typically applied in wastewater regeneration systems.
- The disinfection of urban treated wastewater with Fe anodes and carbon felt cathode is achieved mainly by a combination of chloramination and oxidation by hydrogen peroxide and Fenton's reaction. The efficiency of the system in terms of disinfection rate is comparable to that obtained with CDA. Simultaneously, it is possible to completely eliminate the turbidity of the target effluent and therefore, a reclaimed water for different purposes is obtained.
- In terms of power consumption, iron is the most appropriate anode material to carry out the electrodisinfection process at very low current densities and CDA is the most suitable for the process at current densities higher than 5 A m⁻².

Acknowledgements

The authors acknowledge funding support from the National Spanish Ministry of Education and Science (Project CTM2010-18833). Financial support of the Spanish Government and EU through project FEDER 2007–2013 PP201010 (Planta Piloto de Estación de Estación de Regeneración de Aguas Depuradas) is gratefully acknowledged.

References

- [1] D. Norton-Brandão, S.M. Scherrenberg, J.B. van Lier, J. Environ. Manage. 122 (2013) 85–98.
- [2] B. Salgado, K. Majamaa, J. Sanz, J. Molist, Desalin. Water Treat. 51 (2012) 1519–1526.
- [3] A. Mackie, M. Woszczynski, H. Farmer, M.E. Walsh, G.A. Gagnon, Water Environ. Res. 81 (2009) 1406–1418.
- [4] R. Gori, C. Lubello, F. Ferrini, F.P. Nicese, E. Coppini, Water Sci. Technol. (2008) 883–889.
- [5] R. Iglesias, E. Ortega, G. Batanero, L. Quintas, Desalination 263 (2010) 1–10.

- [6] J. Rodríguez-Chueca, M.I. Polo-López, R. Mosteo, M.P. Ormad, P. Fernández-Ibáñez, *Appl. Catal., B: Environ.* 150–151 (2014) 619–629.
- [7] P.O. Pedersen, E. Brodersen, D. Cecil, *Water Sci. Technol.* 68 (2013) 1852–1856.
- [8] G. Uslu, A. Demirci, J.M. Regan, *Disinfection of Synthetic Municipal Wastewater Effluent by Pulsed UV-Light Treatment*, American Society of Agricultural and Biological Engineers (ASABE), Kansas City, MO, 2013, pp. 948–958.
- [9] U. Nielsen, C. Hastrup, M.M. Klausen, B.M. Pedersen, G.H. Kristensen, J.L.C. Jansen, S.N. Bak, J. Tuerk, *Water Sci. Technol.* 67 (2013) 854–862.
- [10] M.B. Fisher, C.R. Keenan, K.L. Nelson, B.M. Voelker, *J. Water Health* 6 (2008) 35–51.
- [11] W. Yang, D. Zhu, S.Y. Sui-Yi, B.Y. Chen, M.X. Huo, J.W. Li, *J. Water Health* 10 (2012) 557–564.
- [12] A. Kauppinen, J. Ikonen, A. Pursiainen, T. Pitkänen, I.T. Miettinen, *J. Water Health* 10 (2012) 406–418.
- [13] A. Cano, P. Cañizares, C. Barrera-Díaz, C. Sáez, M.A. Rodrigo, *Chem. Eng. J.* 211–212 (2012) 463–469.
- [14] A. Cano, P. Cañizares, C. Barrera, C. Sáez, M.A. Rodrigo, *Electrochem. Commun.* 13 (2011) 1268–1270.
- [15] L. Zaleschi, C. Sáez, P. Cañizares, I. Cretescu, M.A. Rodrigo, *Desalin. Water Treat.* 51 (2013) 3381–3388.
- [16] E. Lacasa, E. Tsolaki, Z. Sbokou, M.A. Rodrigo, D. Mantzavinos, E. Diamadopoulos, *Chem. Eng. J.* 223 (2013) 516–523.
- [17] H. Bergmann, *GWf, Wasser - Abwasser* 151 (2010) 604–613.
- [18] S. Cotillas, J. Llanos, P. Cañizares, S. Mateo, M.A. Rodrigo, *Water Res.* 47 (2013) 1741–1750.
- [19] A. Özcan, Y. Şahin, A. Savaş Koparal, M.A. Oturan, *J. Electroanal. Chem* 616 (2008) 71–78.
- [20] A.R. Khataee, M. Safarpour, M. Zarei, S. Aber, *J. Electroanal. Chem* 659 (2011) 63–68.
- [21] M. Panizza, A. Barbucci, M. Delucchi, M.P. Carpanese, A. Giuliano, M. Cataldo-Hernández, G. Cerisola, *Sep. Purif. Technol* 118 (2013) 394–398.
- [22] M. Pimentel, N. Oturan, M. Dezotti, M.A. Oturan, *Appl. Catal. B: Environ* 83 (2008) 140–149.
- [23] M. Panizza, M.A. Oturan, *Electrochim. Acta* 56 (2011) 7084–7087.
- [24] I. Sirés, N. Oturan, M.A. Oturan, *Water Res.* 44 (2010) 3109–3120.
- [25] M. Panizza, G. Cerisola, *Water Res.* 43 (2009) 339–344.
- [26] D. Lakshmanan, D.A. Clifford, G. Samanta, *Environ. Sci. Technol.* 43 (2009) 3853–3859.
- [27] R. Daghrir, P. Drogui, *Environ. Chem. Lett.* 11 (2013) 151–156.
- [28] APHA-AWWA-WPCF, *Standard Methods for the Examination of Water and Wastewater*, 20th ed., Washington, DC, 1998.
- [29] A.v. Wilpert, *Z. Anal. Chem* 155 (1957) 378.
- [30] H. Freytag, *Z. Anal. Chem* 171 (1959) 458.
- [31] G. Eisenberg, *Ind. & Eng. Chem. Anal. Edition* 15 (1943) 327–328.
- [32] J. Llanos, S. Cotillas, P. Cañizares, M.A. Rodrigo, *Water Res.* 53 (2014) 329–338.
- [33] A. Sánchez-Carretero, C. Sáez, P. Cañizares, M.A. Rodrigo, *Chem. Eng. J.* 166 (2011) 710–714.
- [34] M.J. Farré, S. Day, P.A. Neale, D. Stalter, J.Y.M. Tang, B.I. Escher, *Water Res.* 47 (2013) 5409–5421.
- [35] J.J. Wang, X. Liu, T.W. Ng, J.W. Xiao, A.T. Chow, P.K. Wong, *Water Res.* 47 (2013) 2701–2709.
- [36] G. Pérez, J. Saiz, R. Ibáñez, A.M. Urtiaga, I. Ortiz, *Water Res.* 46 (2012) 2579–2590.
- [37] G.C. White, *Handbook of Chlorination and Alternative Disinfectants*, 4th ed, John Wiley & Sons, Inc, USA, 1999.
- [38] H. Bergmann, A.T. Koparal, A.S. Koparal, F. Ehrig, *Microchem. J.* 89 (2008) 98–107.
- [39] M.E.H. Bergmann, J. Rollin, T. Iourtchouk, *Electrochim. Acta* 54 (2009) 2102–2107.
- [40] A.M. Polcaro, A. Vacca, M. Mascia, S. Palmas, J. Rodriguez Ruiz, *J. Appl. Electrochem.* 39 (2009) 2083–2092.
- [41] B. Crump, W.R. Ernst, H.M. Neumann, *AIChE J.* 44 (1998) 2494–2500.
- [42] P.V. Nidheesh, R. Gandhimathi, *Desalination* 299 (2012) 1–15.
- [43] E. Mohora, S. Rončević, B. Dalmacija, J. Agbaba, M. Watson, E. Karlović, M. Dalmacija, *J. Hazard. Mater* 235–236 (2012) 257–264.
- [44] E. Ortega-Gómez, M.M. Ballesteros Martín, B. Esteban García, J.A. Sánchez Pérez, P. Fernández Ibáñez, *Appl. Catal. B: Environ* 148–149 (2014) 484–489.
- [45] E. Brillas, I. Sires, M.A. Oturan, *Chem. Rev.* 109 (2009) 6570–6631.
- [46] I. Sirés, E. Brillas, *Environ. Int.* 40 (2012) 212–229.
- [47] J. Duan, J. Gregory, *Adv. Colloid Interface Sci.* 100–102 (2003) 475–502.
- [48] P. Cañizares, C. Jiménez, F. Martínez, M.A. Rodrigo, C. Sáez, *J. Hazard. Mater.* 163 (2009) 158–164.